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FIFTH QUARTERLY SUMMARY REPORT

"Mechanism Studies with Boronhydrides"

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I. Introduction

The studies carried out during the Fifth Quarter were mainly concerned with the following topics:

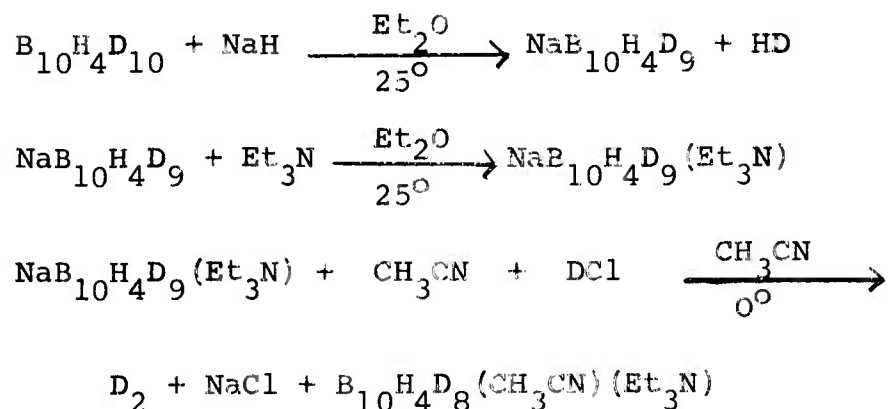
- (1) Mechanism of $B_{10}H_{10}^{-2}$ formation.
- (2) Mechanism of ligand displacement reactions with $B_{10}H_{13}$ (ligand) substrates.
- (3) Elucidation of the stereo-electronic properties of the $C_2B_{10}H_{11}^-$ group.

II. Mechanism of $B_{10}H_{10}^{-2}$ Ion Formation

The work outlined in the Third and Fourth Quarterly Summary Reports has been continued with $B_{10}H_{12}(CH_3CN)(Et_3N)$ as the reaction substrate. Considerable quantities of $B_{10}H_{14}-d_{10}$ have been prepared by the exchange reaction of $B_{10}H_{14}$ with DCl in dioxane solution.¹

(1) J.A. Dupont and M.F. Hawthorne, J. Am. Chem. Soc., 84, 1804(1962).

This procedure yields $B_{10}H_4-d_{10}$ with deuterium at the open face of the icosahedral $B_{10}H_{14}$ fragment. This isotopically labeled decaborane will be converted to the correspondingly deuterated $B_{10}H_{12}(CH_3CN)(Et_3N)-d_8$ derivative by the sequence shown below:



The substrate $B_{10}H_4D_8(CH_3CN)(Et_3N)$ will be examined kinetically with triethylamine in acetonitrile and in benzene solution. If a sizeable primary kinetic isotope appears it may be concluded that

B-H bond breaking is indeed involved in the second step of the overall reaction sequence which leads to $B_{10}H_{10}^{-2}$.

III. Mechanism of Ligand Displacement Reactions with $B_{10}H_{13}$ (ligand) Substrates.

Work on this problem has recently centered about the optical resolution of the $B_{10}H_{13}[N(CH_2\phi)(Et)(Me)]$ anion which contains an asymmetric nitrogen atom. Dissociation of this group during the displacement reaction would lead to racemization at nitrogen. To date only partial resolution has been obtained and optical rotations are too low to permit kinetic experiments.

IV. Elucidation of the Stereo-Electronic Properties of the $C_2B_{10}H_{11}^-$ Group.

The nitration of phenylcarborane ($\phi C_2B_{10}H_{11}$) with mixed acid at 80° produces a 50:50 mixture of m- and p-nitrophenylcarboranes. Separation of these isomers followed by catalytic hydrogenation produced the corresponding anilines in quantitative yield. The m- and p-aminophenylcarboranes will be examined as substrates in representative reactions with known (or easily determined) rho values. In this manner σ values for the carborane nucleus may be obtained. Further work will involve the determination of the solvolysis rate constants for m- and p-carboranyl benzyl halides.

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